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Conformation of Polyaniline: Effect of Mechanical Shaking and Spin
Casting

by

J. Feng, A.G. MacDiarmid, and A.J. Epstein

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The Ohio State University
Department of Physics
Columbus, OH

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J. Feng, A.G. MacDiarmid, and A.J. Epstein

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Department of Physics
The Ohio State University
174 West 18th Avenue
Columbus, OH 43210-1106

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We find from diffuse reflectance Vis/UV spectral studies of polyaniline (emeraldine base; EB) powder doped with camphorsulfonic acid (HCSA) that the free carrier tail characteristic of an extended coil conformation appears and increases gradually on mechanical shaking with KBr powder. We also find that the forces present during spin-casting of EB films have a significant effect on the value of the absorption maximum of the exciton peak.

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Conformation of polyaniline: effect of mechanical shaking and spin casting

J. Feng^a, A. G. MacDiarmid^a and A. J. Epstein^b^a Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA^b Department of Physics, The Ohio State University, Columbus, OH 43210-1106, USA**Abstract**

We find from diffuse reflectance Vis/UV spectral studies of polyaniline (emeraldine base; EB) powder doped with camphorsulfonic acid (HCSA) that the free carrier tail characteristic of an extended coil conformation appears and increases gradually on mechanical shaking with KBr powder. We also find that the forces present during spin-casting of EB films have a significant effect on the value of the absorption maximum of the exciton peak.

Keywords: Polyaniline and derivatives; Reflection spectroscopy; UV-Vis-NIR absorption; Spin casting

1. Introduction

It has been previously reported [1] that a conformational change of doped polyaniline results in an electronic spectral change. Thin films of polyaniline doped with camphorsulfonic acid (HCSA) spun from chloroform solution showed a localized polaron absorption at ~800nm. This localized polaron absorption characterizes the coil-like conformation of doped polyaniline. For doped polyaniline with an extended coil conformation, such as HCSA-doped polyaniline in *m*-cresol solution, the ~800nm peak disappears and is replaced by a very intense free carrier tail starting at ~1000nm and increasing steadily in intensity to ~2600nm. This is consistent with delocalization of electrons in the polaron band promoted by a "straightening-out" of the polymer chain as its coil-like structure becomes more expanded with concomitant reduction in π -defects caused by ring twisting.

It was also found that the compact coil to expanded coil conformational change with accompanying change in its Vis/UV spectrum could be effected by mechanical stretching of a polyaniline/PVC blend film [1]. This kind of "mechanochromic" effect was also found in polyaniline coatings made from dispersion of polyaniline in a non-conductive matrix [2]. In this study, we present further results on the effect of mechanical stress on the molecular conformation of polyaniline.

2. Experimental

All chemicals were purchased from Aldrich Co. Camphorsulfonic acid (HCSA, 98%) was used as received. Potassium bromide (KBr) powder was FTIR grade. N-Methylpyrrolidinone (NMP) and chloroform were HPLC grade.

UV/Vis/NIR spectral studies were carried out on a Lambda 9 UV/Vis/NIR spectrophotometer (Perkin Elmer Co.). The diffuse reflectance spectra were recorded with a 60mm integrating sphere attachment (Perkin Elmer Co.) [3].

Polystyrene vials (1/2 in. diameter x 1 in. long) with a polyethylene slip-on cap, Plexiglas ball pestles (3/8 in. diameter) and heavy-duty Wig-L-Bug grinder/mixer for shaking were purchased from Aldrich Co.

Polyaniline powder (emeraldine base, EB) was synthesized following a well established procedure [4].

A series of different concentrations, ranging from 0.4 wt.% to 5.0 wt.% and also one at 20 wt.%, of EB in NMP was made

by dissolving fine EB powder in NMP with constant stirring at room temperature. The thin spun films were cast on cover glass slides by using a spinning machine (Headway Research Inc.). Free standing thin films were made by dropping a few drops of the prepared solution on the cover glass slides. They were spread over the whole slide without spinning. The films were dried in a desiccator under dynamic vacuum. Gelled films were prepared by placing the 20% solution between two glass slides. The thick paste was then smeared in one direction by lateral movement of the slides to make the gelled film thin enough for UV/Vis measurements.

A HCSA-doped Pani stock solution was made by dissolving 0.0901g of EB powder in chloroform containing 0.1177g HCSA. It was then stirred at room temperature for 24 hours.

HCSA-doped Pani powder was obtained by pouring the above solution into 1000ml of hexane at room temperature followed by filtration with a Buchner funnel. The dark green powder was held in a desiccator under dynamic vacuum at room temperature for ~4 hours. 5.0mg of this dried HCSA doped Pani powder was put into a polystyrene vial with 0.5g KBr and shaken (Wig-L-Bug) for 30 minutes. The powder was then transferred into a powder cell and the diffuse UV/Vis reflectance spectrum was measured.

0.1ml of the stock solution was slowly spread over 5.0g KBr powder in a vial with gentle stirring. The Pani/HCSA coated KBr powder was dried under dynamic vacuum for 1 hour. The dried KBr powder was transferred into a powder cell for measurement of its diffuse reflectance spectrum. The powder was then transferred into a polystyrene vial and was shaken for various times in the Wig-L-Bug. The diffuse reflectance UV/Vis was then remeasured.

3. Results and Discussions

In order to get electronic spectra of polyaniline powder, diffuse reflectance measurements were used instead of transmittance measurements. Kubelka and Munk developed a reflectance theory and derived a so-called Kubelka-Munk function. Like the Beer-Lambert law used in transmittance spectroscopy, the Kubelka-Munk function is valid only when the material is weakly absorbing [5]. Potassium bromide (KBr) powder was thus chosen to dilute the polyaniline powder by mechanically mixing them thoroughly.

The diffuse reflectance UV/Vis spectrum of HCSA-doped polyaniline powder precipitated from chloroform solution in hexane as previously described and then shaken with KBr powder showed both a localized polaron absorption at $\sim 800\text{nm}$ and a poorly developed free carrier tail shown in Figure 1d. Since HCSA-doped polyaniline in chloroform solution does not show a free carrier tail in its UV/Vis spectrum and hexane is a nonsolvent for the polyaniline, it is *unexpected* to find a free carrier tail in the UV/Vis spectrum of this polyaniline powder. Thus we concluded that mechanical shaking alters the diffuse UV/Vis reflectance spectrum of doped polyaniline powder. As shown in Figure 1a, the diffuse reflectance UV/Vis spectrum of HCSA-doped polyaniline powder dispersed on solid KBr, *without any mechanical agitation*, was essentially identical to its solution transmittance UV/Vis spectrum [1]. However, after this mixture was shaken, a free carrier tail appeared and increased gradually with shaking time (see Figures 1b and 1c). This trend is consistent with increasing delocalization of electrons in the polaron band promoted by shearing forces which straighten out the polymer chain from its tight coil conformation to a more expended coil conformation.

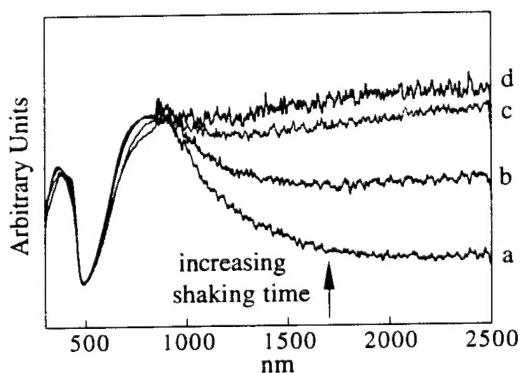


Figure 1. Diffuse reflectance Vis/UV spectra of HCSA-doped Pani powder with different shaking times: a, 0 min; b, 5 mins; c, 10 mins; d, 30 mins

A similar mechanochromic effect was also found with undoped polyaniline (EB) thin films *spun cast* from NMP solution. We found that solutions of polyaniline (emeraldine base, EB) in NMP (0.4 to 5.0% wt/v) have a constant exciton absorption at $\sim 637\text{nm}$ but that thin films spun cast from these solutions exhibit absorptions in the range $\sim 650\text{nm}$ to $\sim 615\text{nm}$. However, films formed *without spinning* had absorptions at $\sim 625\text{nm}$. It is postulated that the forces present during spinning are responsible for this effect. This mechanochromic effect was reduced by exposing the thin spun films to NMP vapor for 0.5 hour as shown in Figure 2.

The thin film spun from 0.8 wt.% solution could be completely dissolved in NMP while a spun thin film from a 5.0 wt.% solution was only partially soluble. The insoluble part showed an exciton absorption at $\sim 638\text{nm}$. The gelled film from the 20 wt.% solution showed an abnormal exciton absorption at $\sim 711\text{nm}$ and was only partially soluble. The insoluble part of this gelled film showed an exciton absorption at $\sim 640\text{nm}$.

The above results are consistent with the fact that shearing forces can disentangle polymer chains and orient polymer chains [6]. There is more entanglement of polymer chains in concentrated solutions which promotes gelation and decreases solubility in NMP. Upon spinning, the only slightly entangled polymer chains (from dilute solutions) are disentangled and oriented under shearing forces. The alignment of polymer chains reduces defects from ring twisting

resulting in a decrease of exciton absorption energy. Since there is less entanglement between chains, there are fewer crystalline and/or gelation sites. The polymer easily forms amorphous regions which are dissolved in NMP solution. Since NMP is a good solvent for polyaniline, the polymer chain tends to relax back to its conformation present in solution on exposure to NMP vapor.

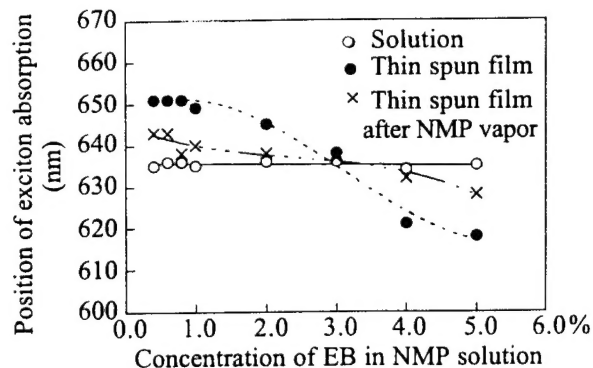


Figure 2. λ_{max} of exciton peak of EB as a function of NMP treatment (see text)

On the other hand, the heavily entangled polymer chains (from concentrated solutions) are barely disentangled by spinning and hence are only slightly oriented under the same conditions. The interaction between polymer chains is increased upon evaporation of NMP. This results a tight coil-like conformation. The tight-coil conformation of polymer chains increases ring twisting and therefore increases the exciton absorption energy. The interaction between polymer chains is reduced on exposure to NMP vapor.

4. Conclusions

Simple shearing forces, such as shaking and spinning, can induce conformational changes of both doped and undoped polyaniline in the solid state. This results in a reduction of defects of the polyaniline chains caused by ring twisting. The resulting "straightening-out" of polyaniline chains delocalizes the electrons in the polaron band in doped polyaniline. The same effect decreases the exciton absorption energy in undoped polyaniline.

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